Vapor/Particle Interactions Measured with an Aerosol Mass Spectrometer (AMS)

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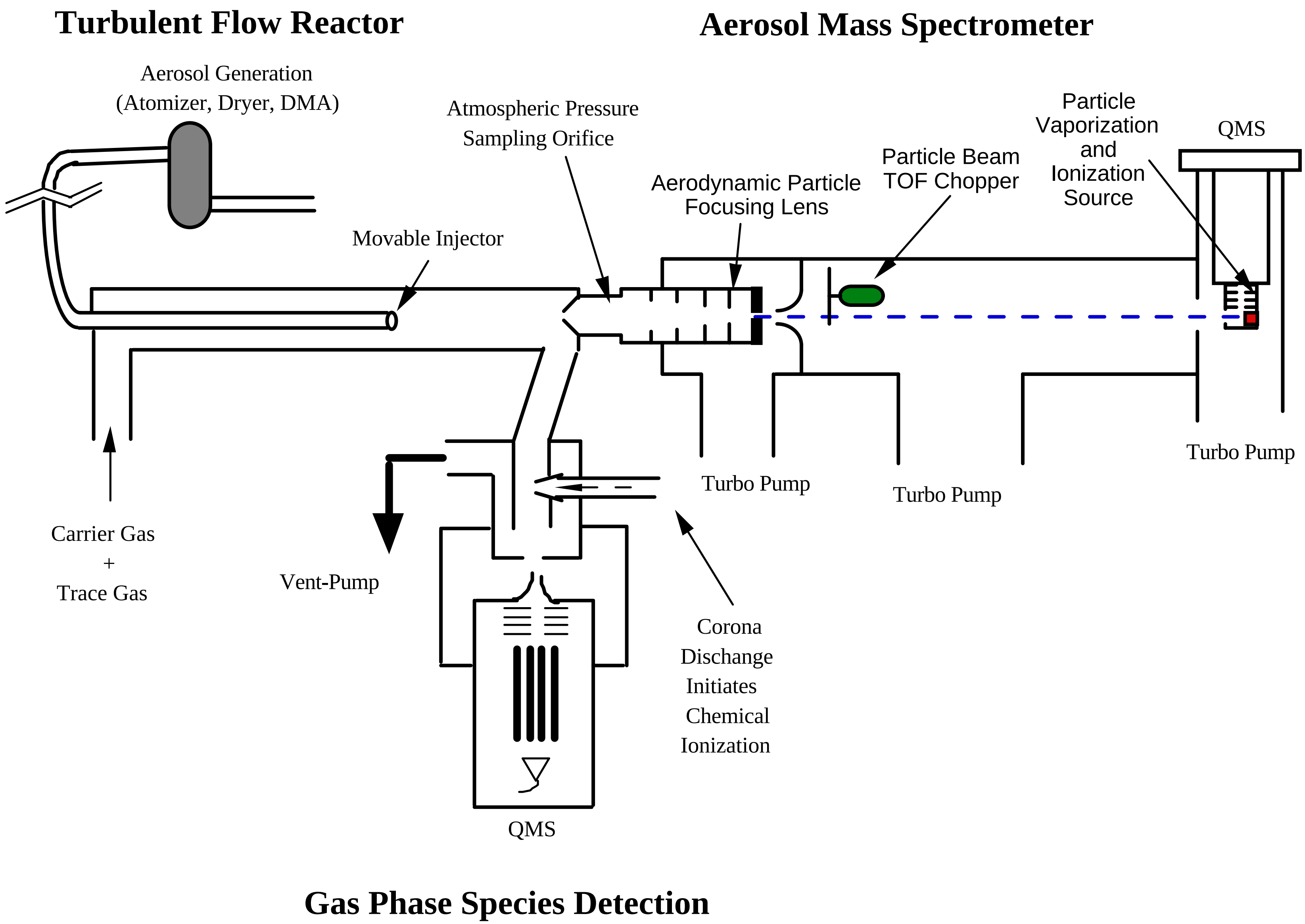

Turbulent Flow Reactor
Aerosol Mass Spectrometer
Aerosol Generation
(Atomizer, Dryer, DMA)
Atmospheric Pressure
Sampling Orifice
Particle
Vaporization
and
Ionization
Source
QMS
Particle Beam
TOF Chopper
Aerodynamic Particle
Focusing Lens
Movable Injector
Turbo Pump
Turbo Pump
Turbo Pump
Carrier Gas
+
Trace Gas
Vent-Pump
Corona
Dischange
Initiates
Chemical
Ionization
QMS
Gas Phase Species Detection

OBJECTIVE: Measure rates of nucleation and growth processes underlying secondary aerosol growth.

PLAN: Couple ARI aerosol mass spectrometer (AMS) with the BC chemical ionization mass spectrometer (CIMS) to provide simultaneous measurement of condensed and particle phases.

Flows of aerosols with known size distributions and composition are monitored with the AMS.

Levels of condensable gases are simultaneously manipulated and monitored with mass spectrometrically (via CIMS).

By quantitatively mixing aerosols of known size (selected with a differential mobility analyzer, DMA) with gases at known concentration for variable times (varying between a fraction of a second and minutes), aerosol growth rates can be determined and expresses as uptake coefficients which than can be applied to atmospheric aerosol models.

The first task is the investigation of kinetics of particle growth by vapor accretion to particles, i.e. determine uptake coefficients, including mass accommodation coefficients and heterogeneous reaction rate coefficients.

Initial experiments have monitored:

Deliquescence of H_2SO_4 aerosols with water,
Condensation of oxalic acid on $(NH_4)_2SO_4$.
Condensation of PAHs on DOP

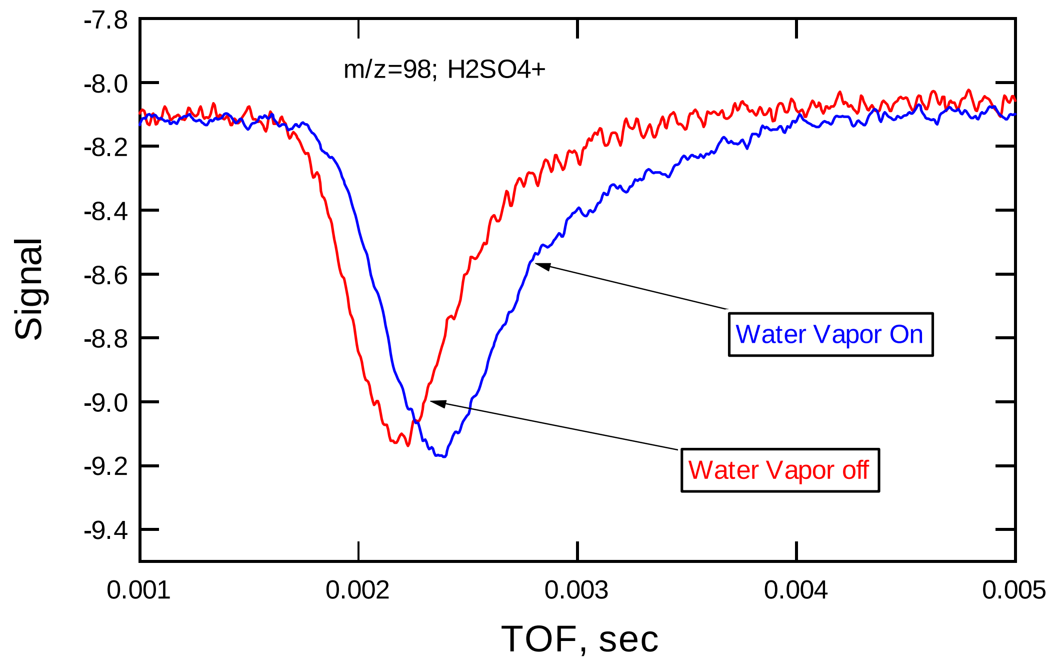
A monodisperse aerosol of 100-300 nm in diameter is selected with the DMA and exposed vapor within the gas/aerosol flow tube for about 3 seconds.

Vapor uptake is clearly resolved by the AMS, indicative of aerosol growth via vapor condensation.

Uptake scales with vapor level.was observed as
Particle diameter increases of 50-100 nm.

Further experiments are in progress to quantify these observed growth rates.

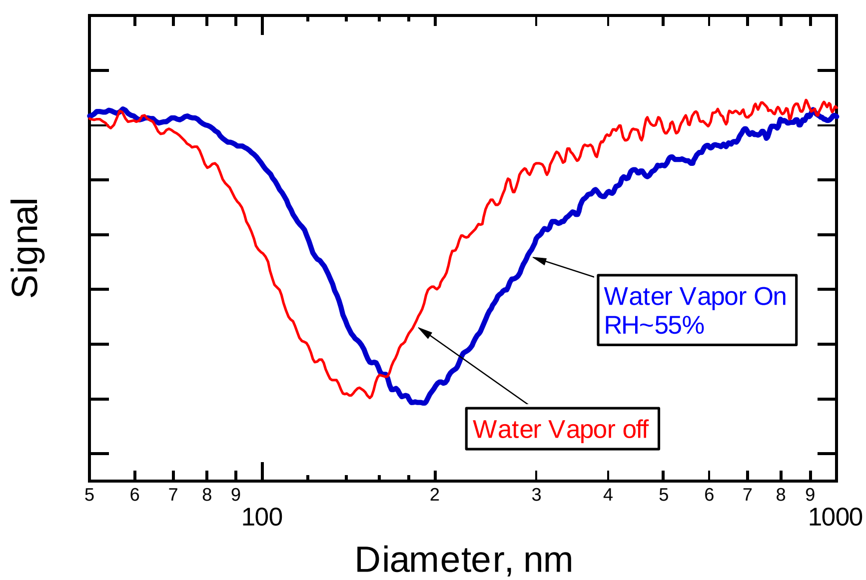
Deliquescence of H_2O onto H_2SO4 Aerosol



Addition of 55% relative humidity leads to

~90wt% to ~35wt%

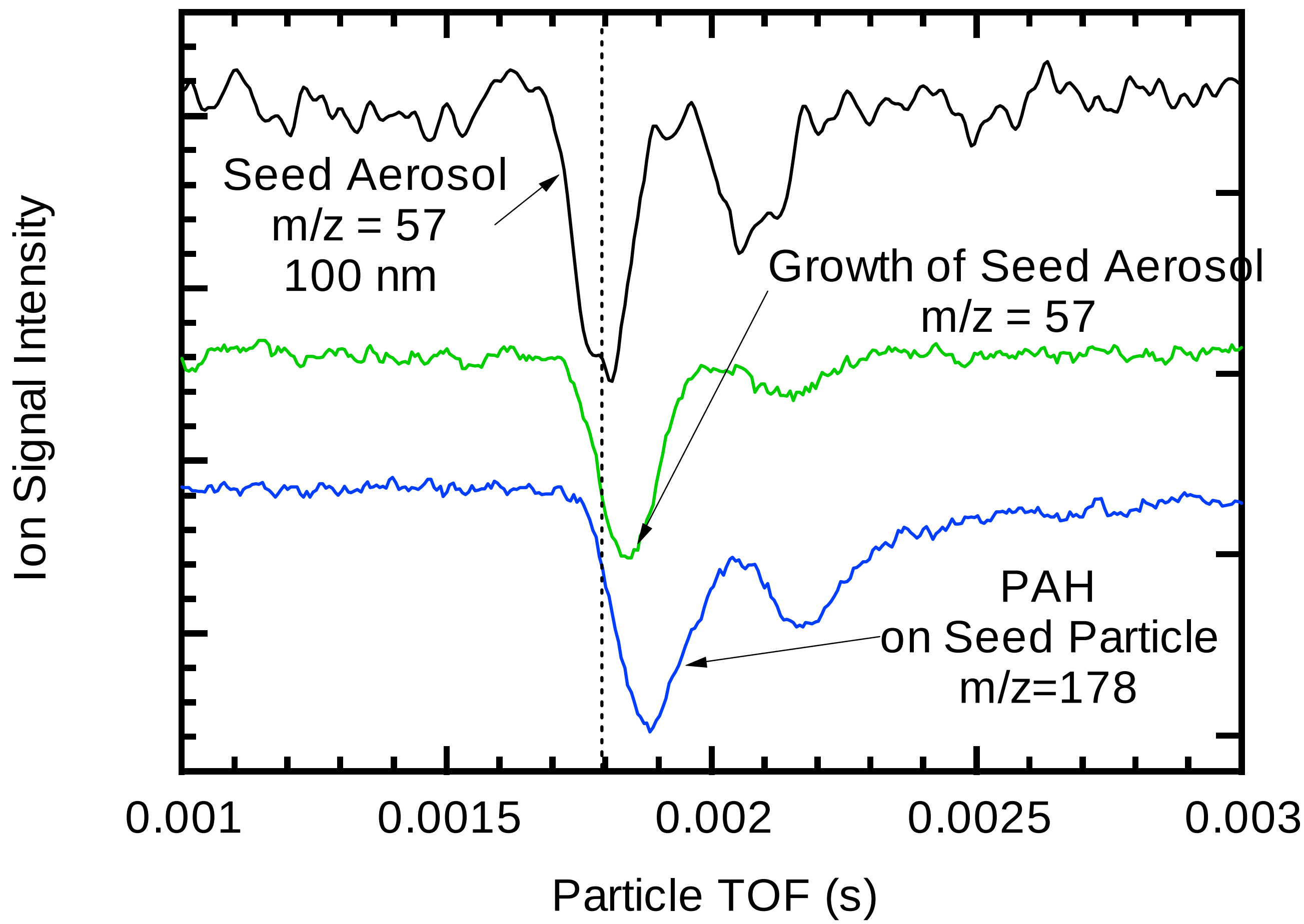
composition change of H_2SO4 aerosol



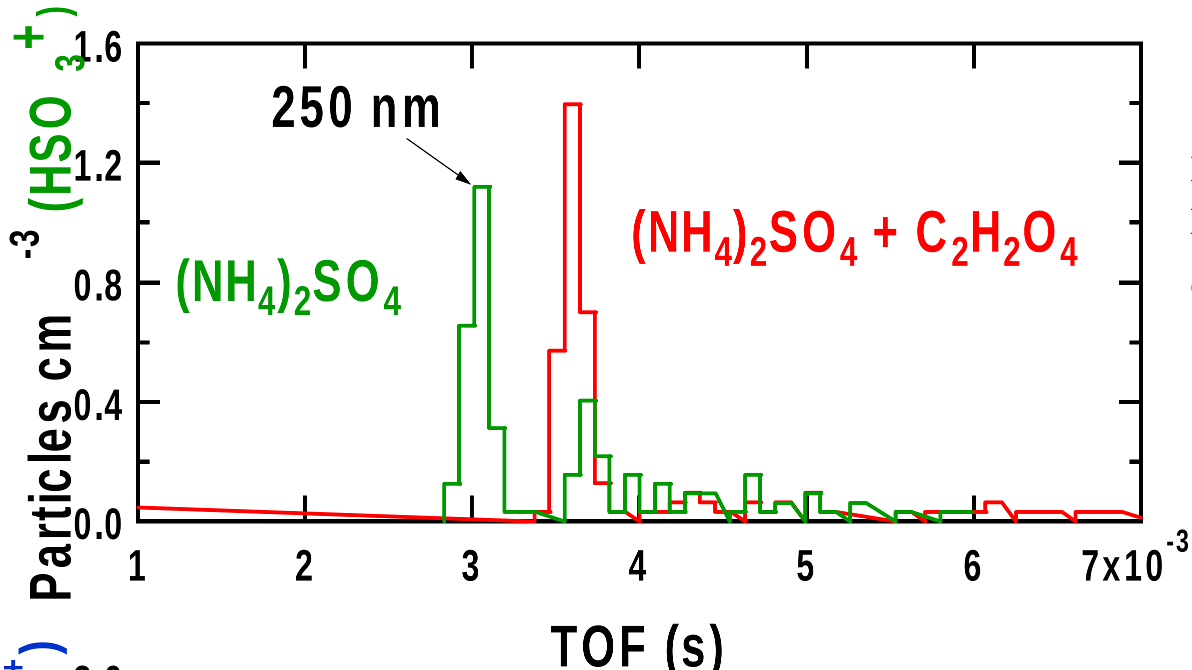
Aerosol growth corresponds to diameter increase of

~150 to 200nm

Condensation of PAH on DOP Aerosol

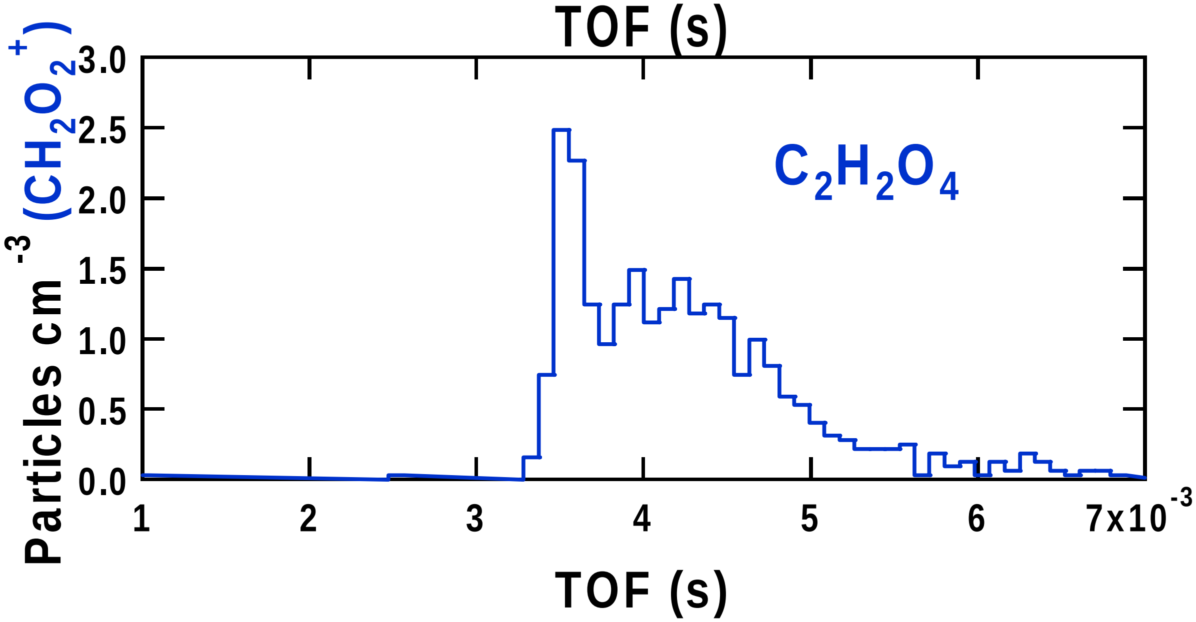


Oxalic Acid Uptake Experiment



DMA pre-sized ammonimum sulfate particles (250 nm diameter) grow when exposed to oxlaic acid vapor.

Particle size is inversely related to particle TOF (see AMS below).



Grown particles also appear as condensed oxalic acid in the mass spectrometer.

Aerosol Mass Spectrometer (AMS) for Size and Composition Analysis of Submicron Particles

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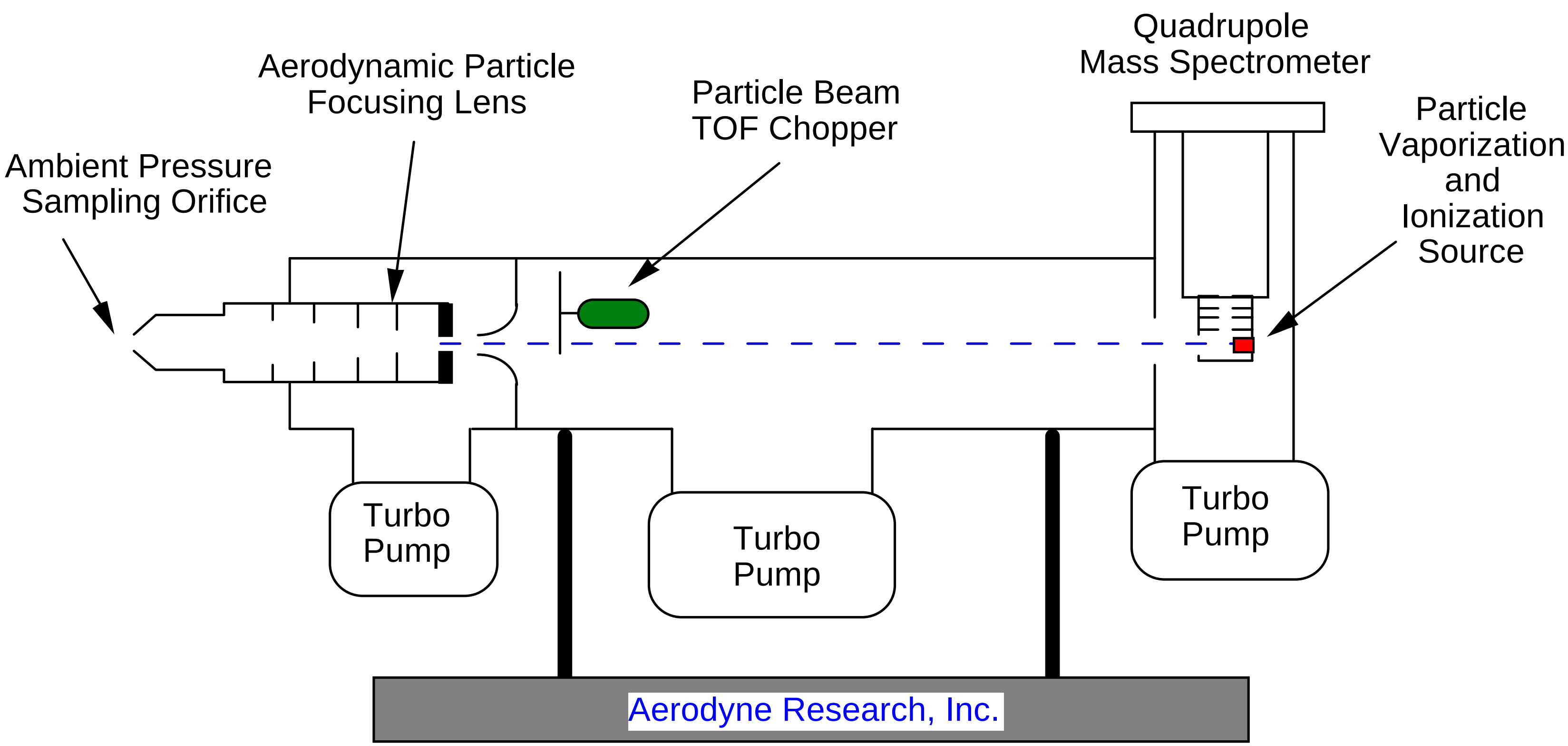
Aerosol Mass Spectrometer for Real-Time Size and Composition Analysis of Submicron Particles

Particle Beam Generation

Aerodynamic Sizing

Particle Composition



INTRODUCTION

A thorough understanding of atmospheric aerosol physical and chemical processes requires knowledge of aerosol *size-resolved chemical composition*.

Over the next decade both laboratory and field measurements will demand instrumentation which can provide this capability.

Ideally such instrumentation should also provide *quantitative* analysis in *real-time*.

The Aerosol Mass Spectrometer (AMS) utilizes an aerodynamic lens to focus particles into high vacuum. Time-of-flight (TOF) velocity measurement determines aerodynamic particle diameter followed by flash vaporization and mass spectrometric chemical analysis.

Numerical Fluid Dynamic Modeling (FLUENT) Predicts:

Narrow Beam Width *(~0.2mm)*

Aerodynamic Velocities *(50-250 ms^{-1})*

100% Particle Collection Efficiency *(50 to 500nm diameter)*

[*~40% to 5μm*]

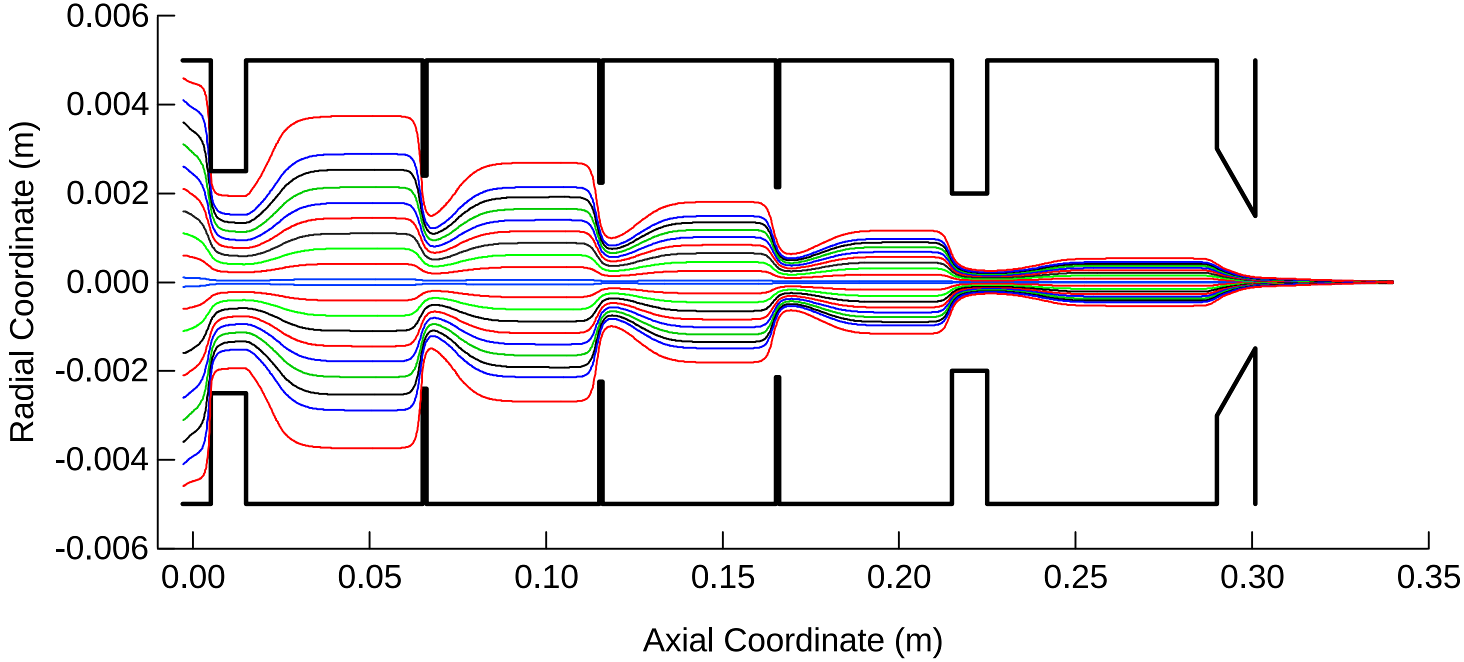
Calibrated with DMS selected particles

Lens Design from University of Minnesota

Liu et al, *Aer. Sci Tech.* 22:293;314 (1995)

Ziemann et al, *J. Aer. Sci.* 26:745 (1995)

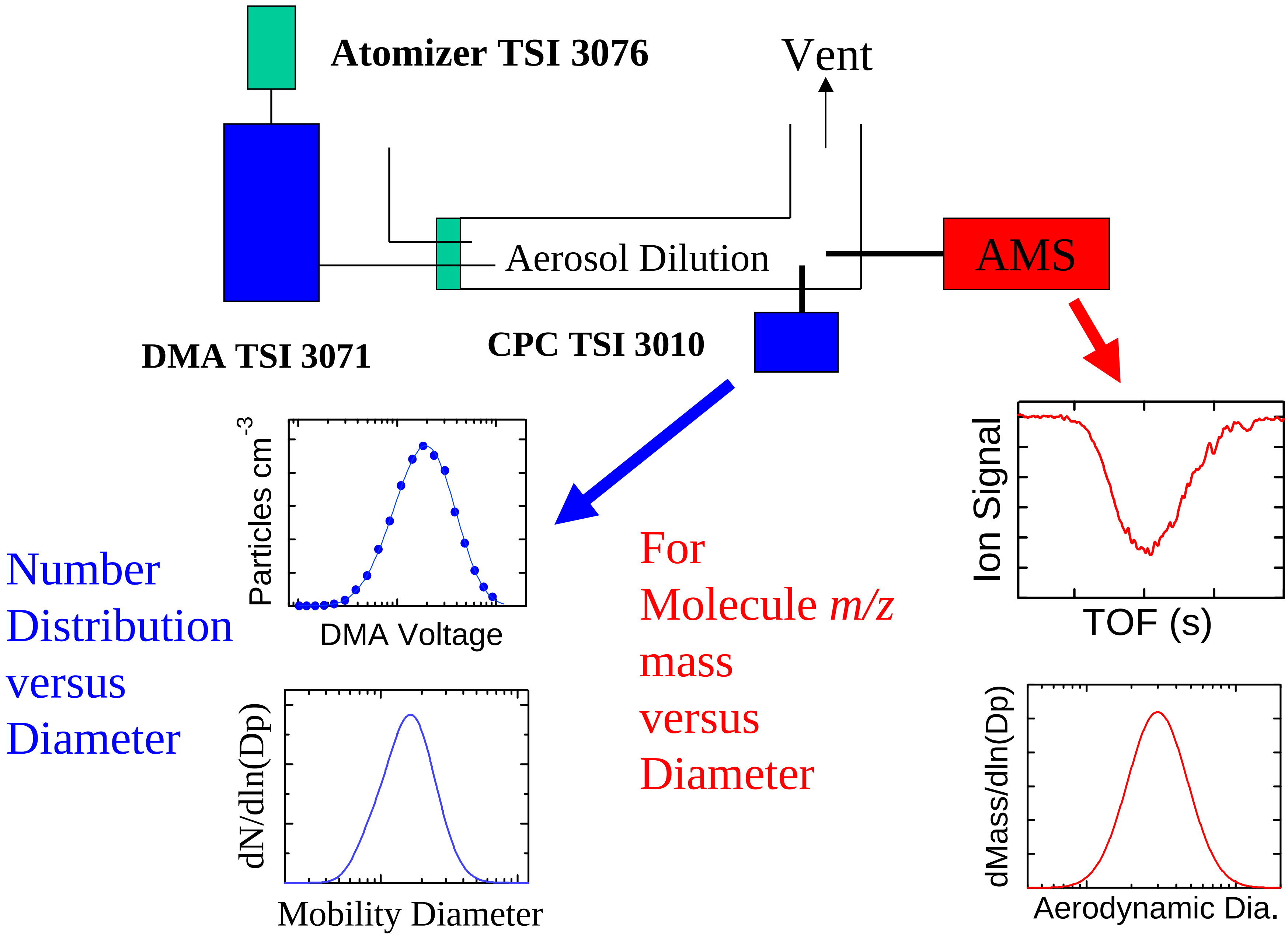
Calculated Particle Trajectories in Aerodynamic Lens
100 nm Diameter Unit Density Spheres
(Fluent ver 4.47)



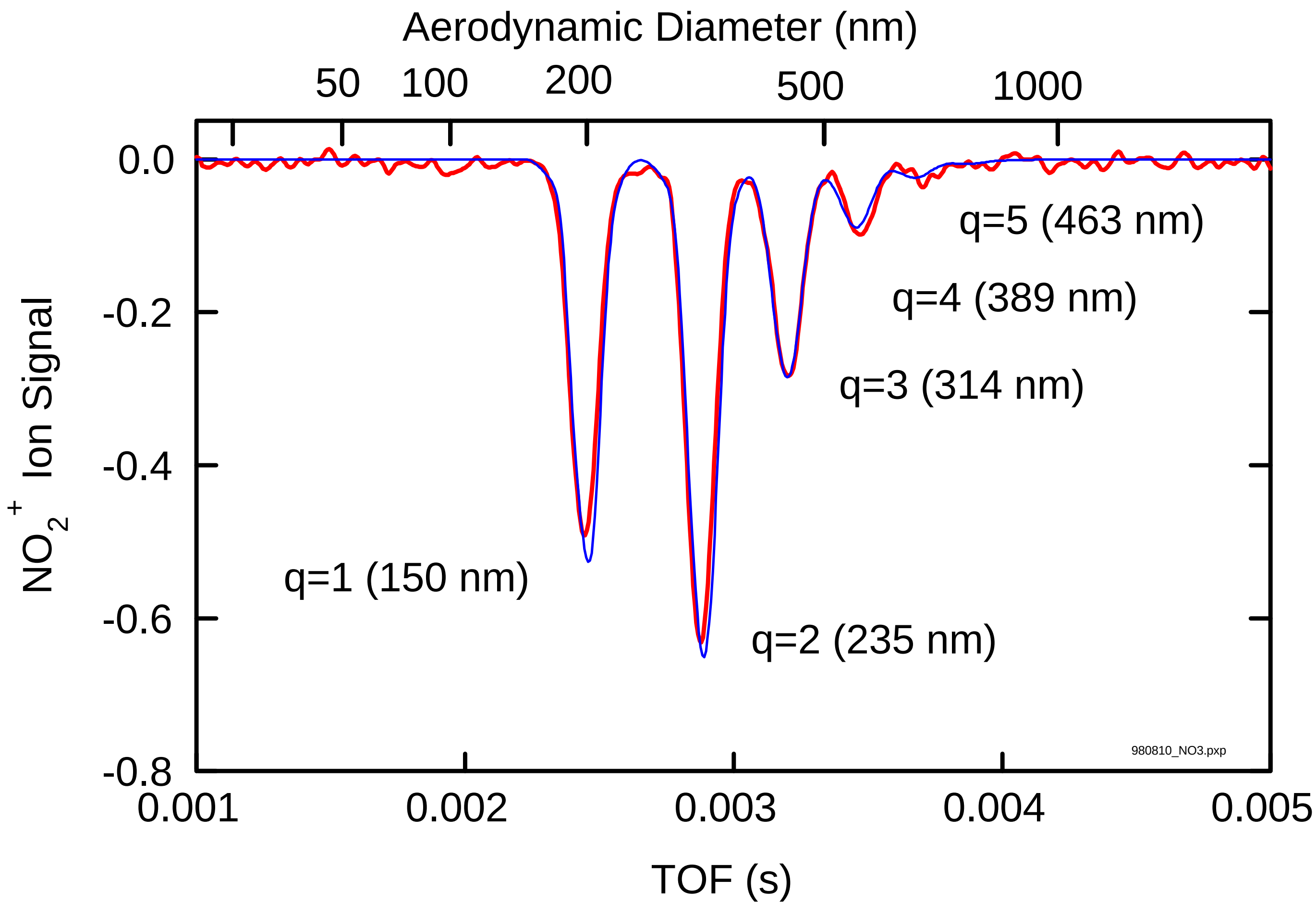
2.4 torr Inlet

10^{-3} torr Exit

AMS-DMA Calibration Setup

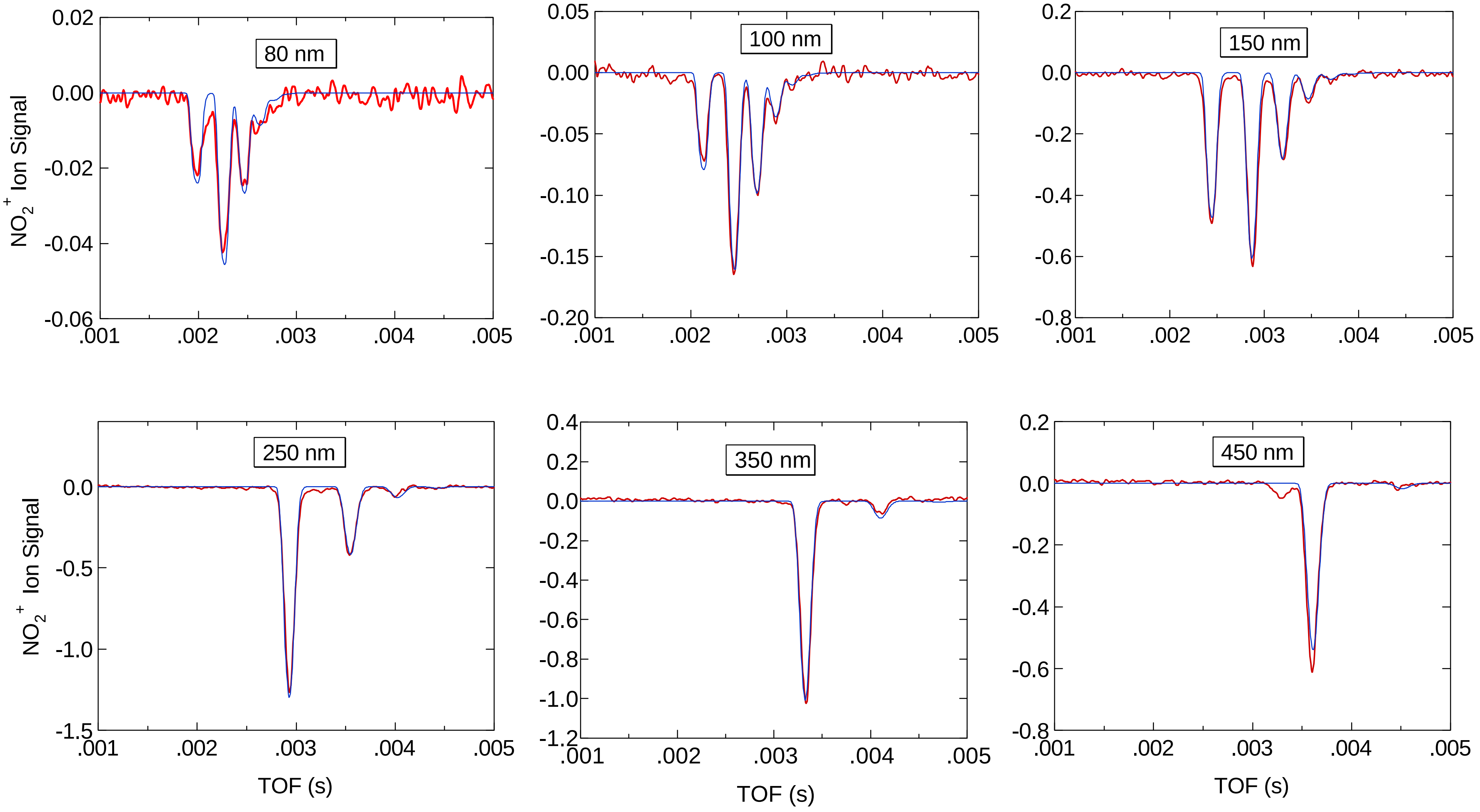


Particle Time-of-Flight (TOF) Spectra for NH_4NO_3 Particles Pre-Sized by the DMA

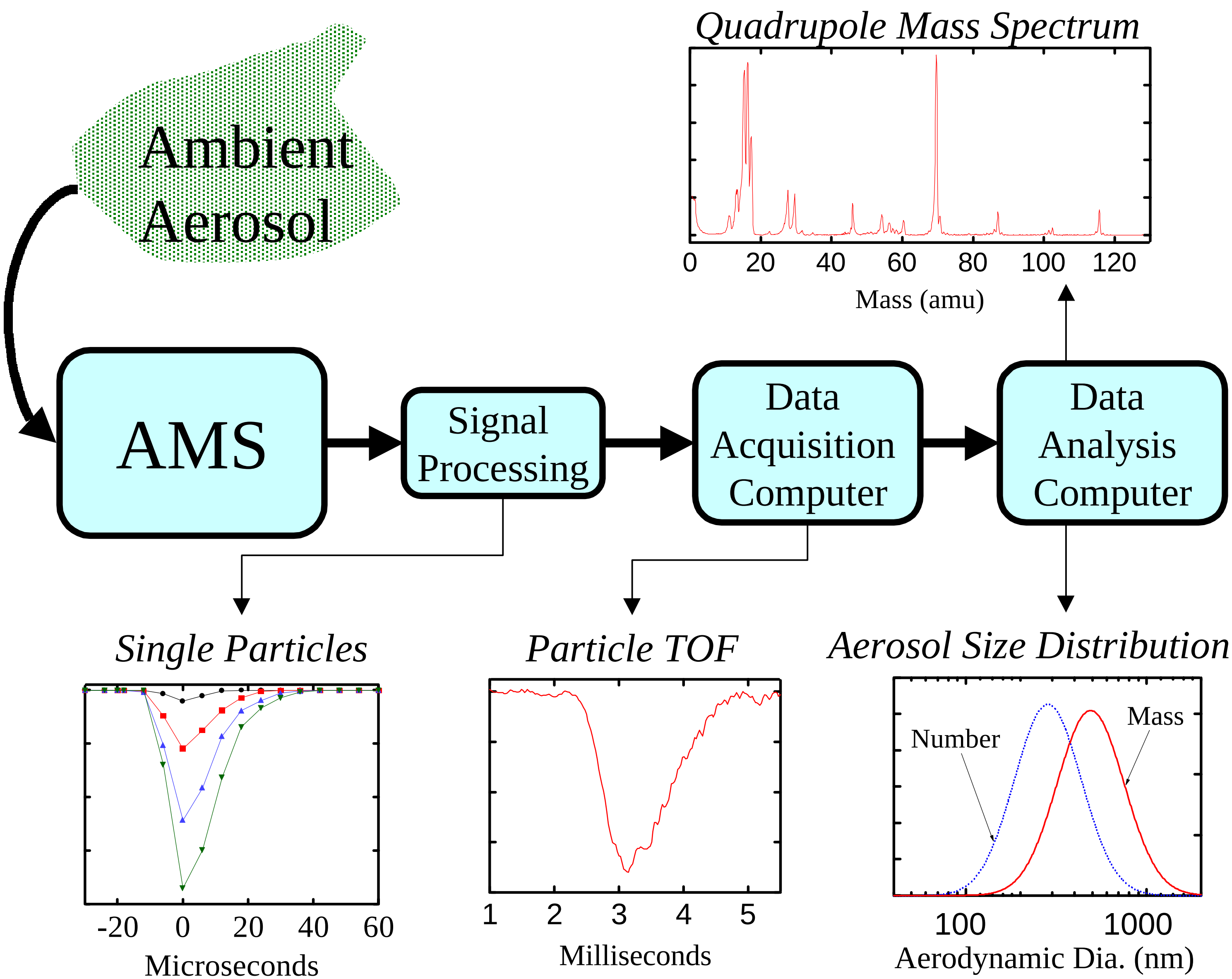


MODEL LINE accounts for: 1) The DMA transfer function,
2) The AMS particle collection efficiency and transfer function, and
3) linear mass detection for an input polydisperse input aerosol distribution

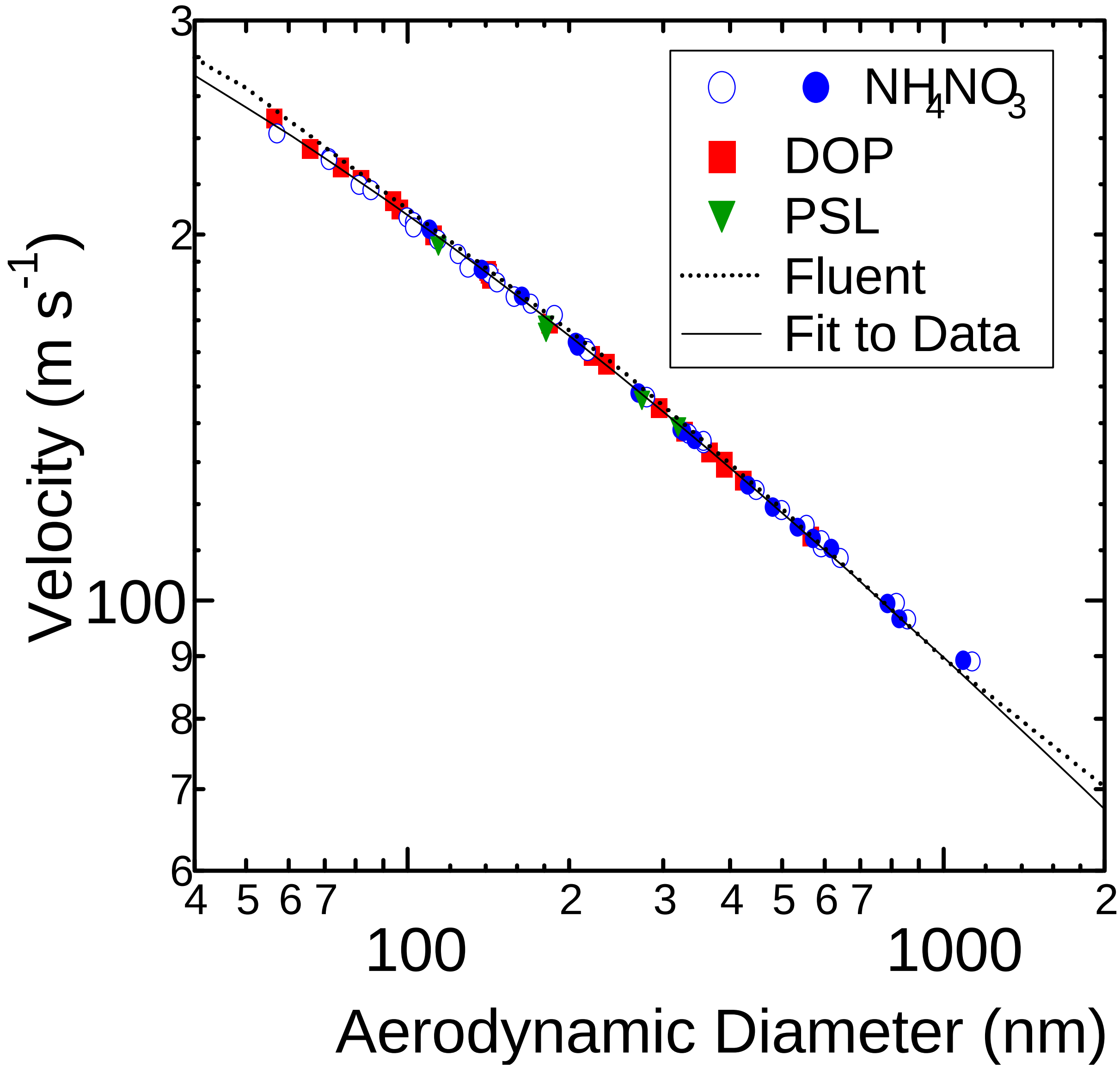
AMS TOF Calibration for DMA Selected NH_4NO_3 Particles



Real Time Aerosol Measurement and Data Processing



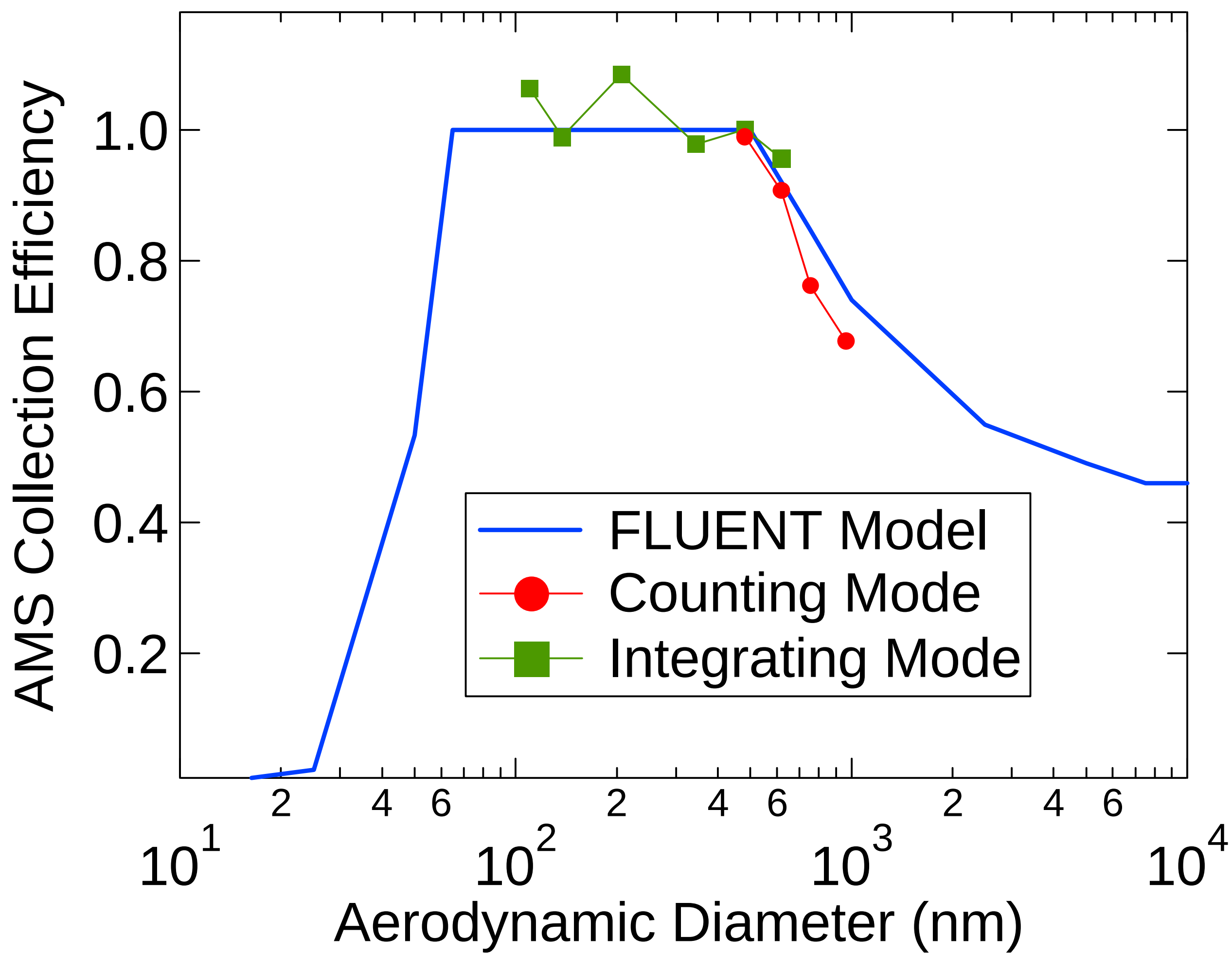
Particle Velocity-Aerodynamic Diameter Calibration



$$vel = \frac{v_g}{1+(D_{aero}/D_*)^b}$$

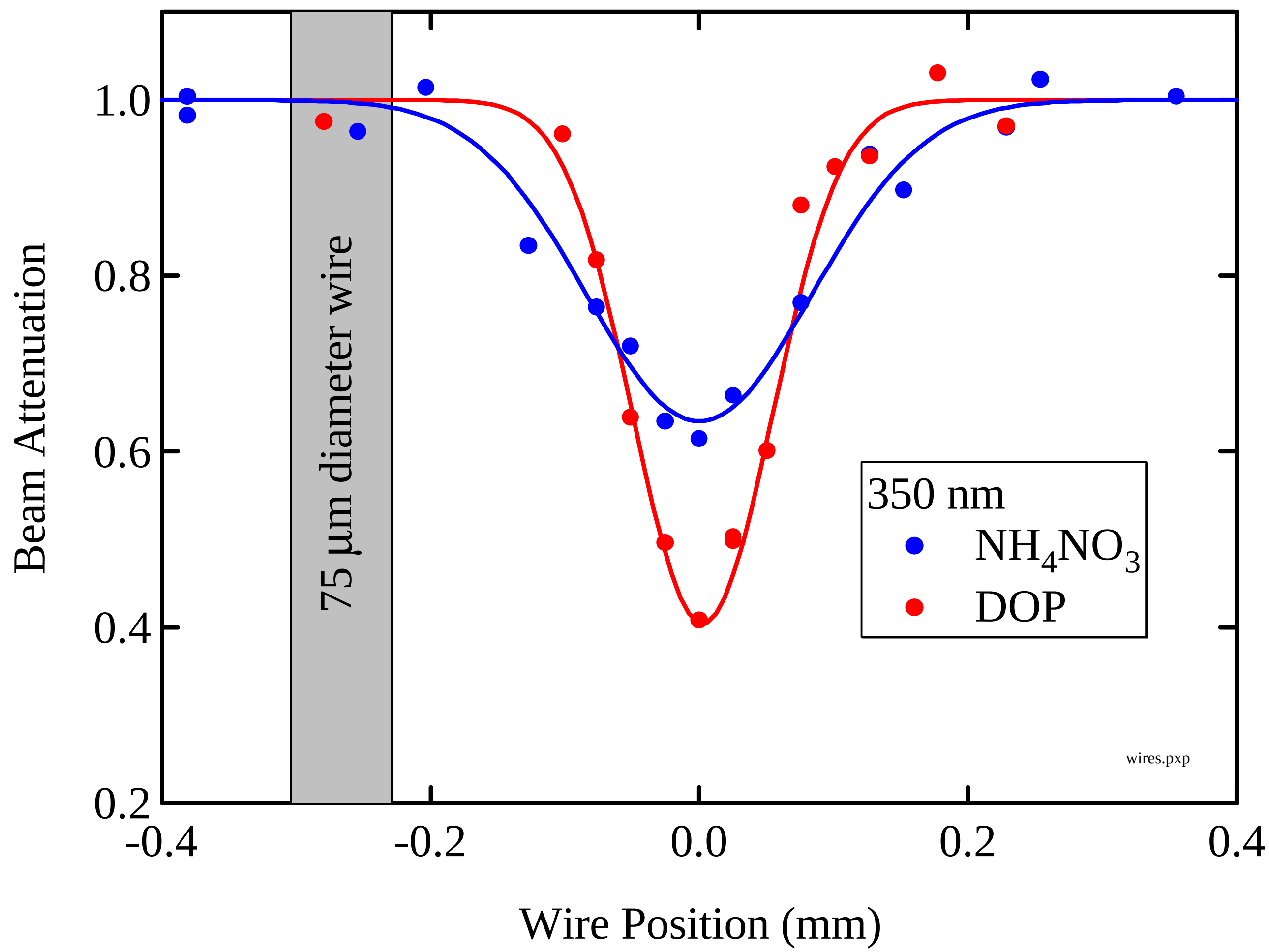
$$D_{aero} = D_{geom} * Density * ShapeFactor$$

Measured Particle Collection Efficiencies Compared to FLUENT Model Prediction



NH_4NO_3

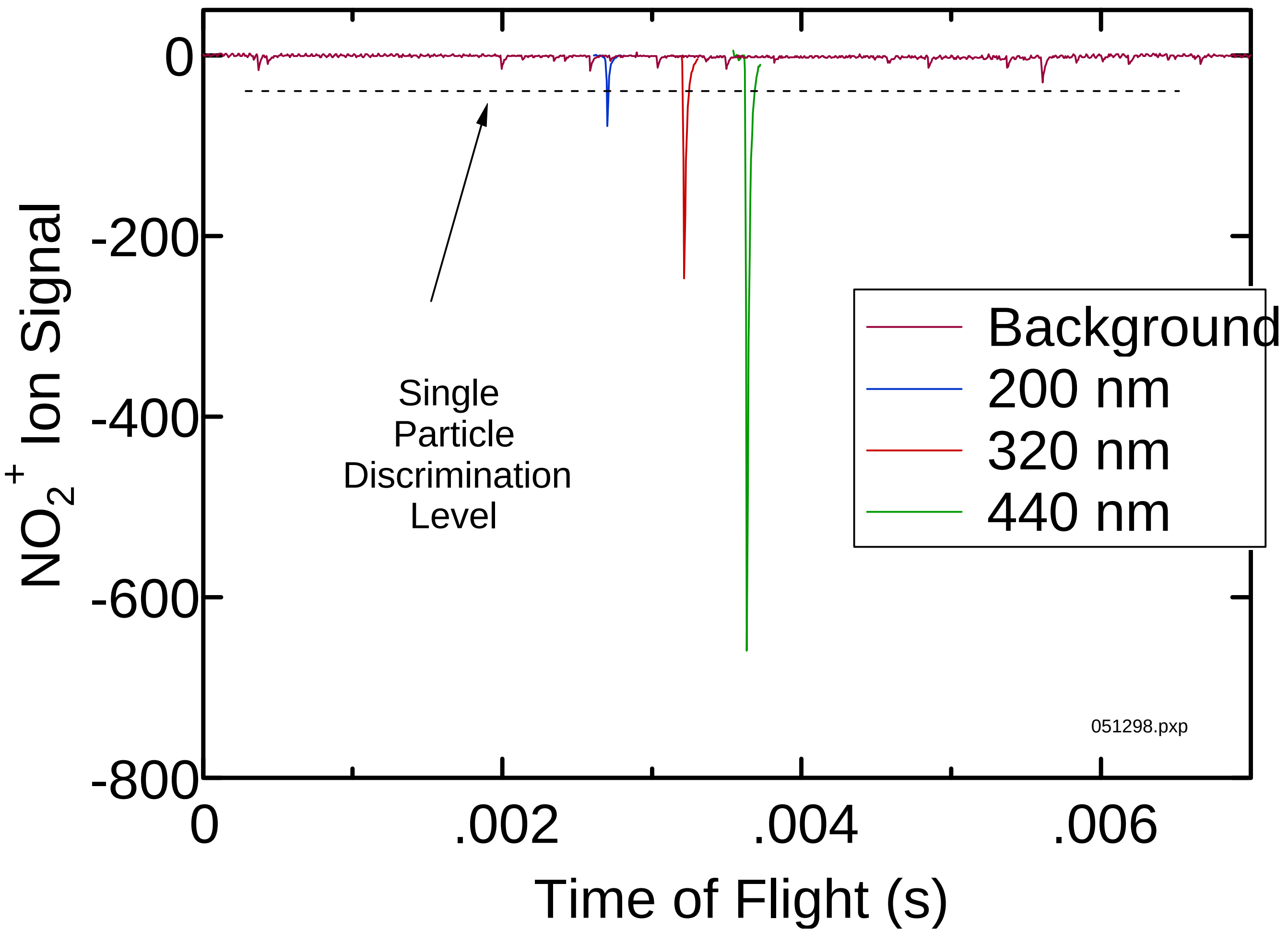
Narrow Particle Beam Width *(~0.2mm)*



16 cm pathlength

Variable beam width
dependent on particle morphology

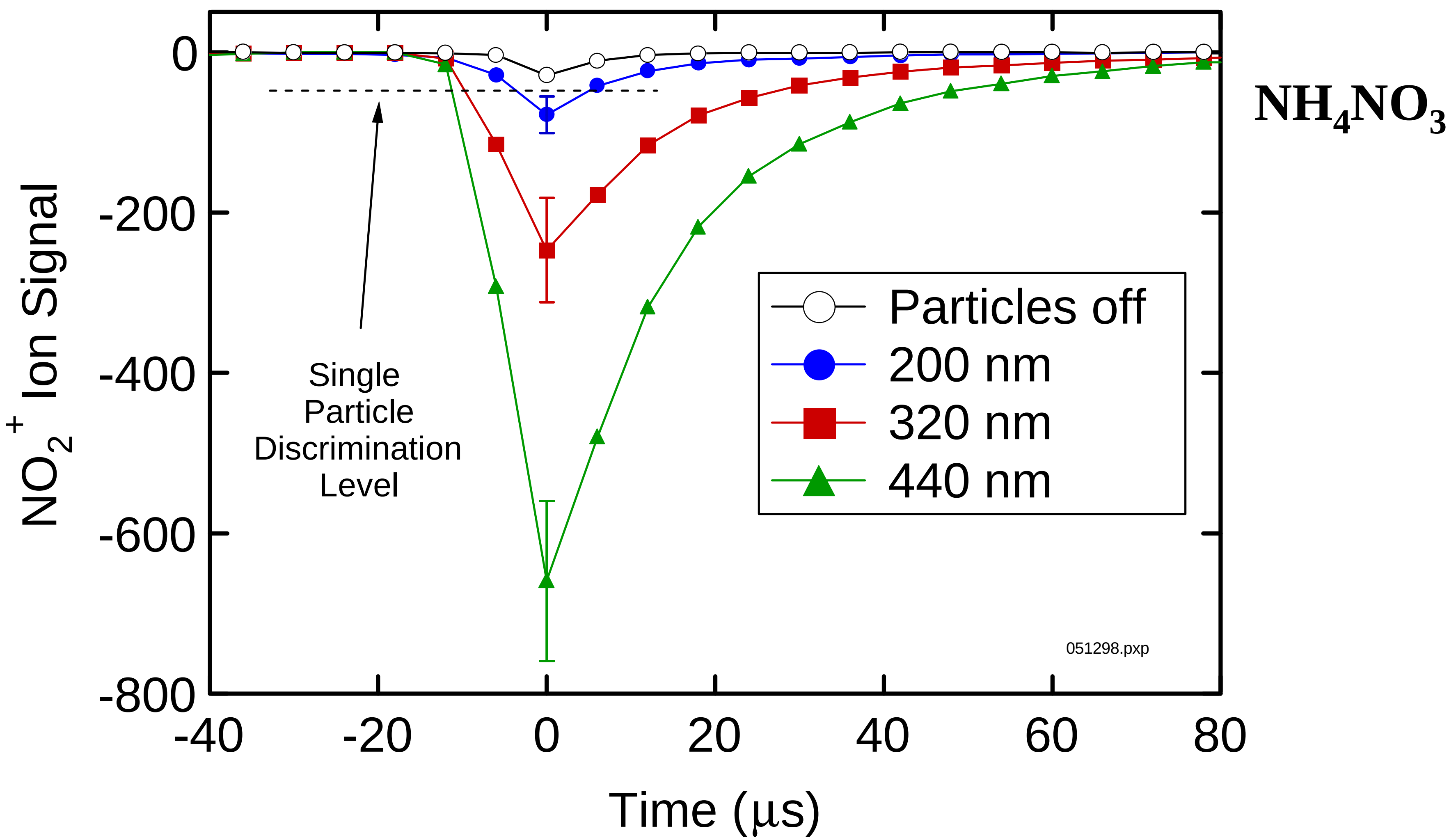
Time Resolved Single Particle Detection



NH_4NO_3

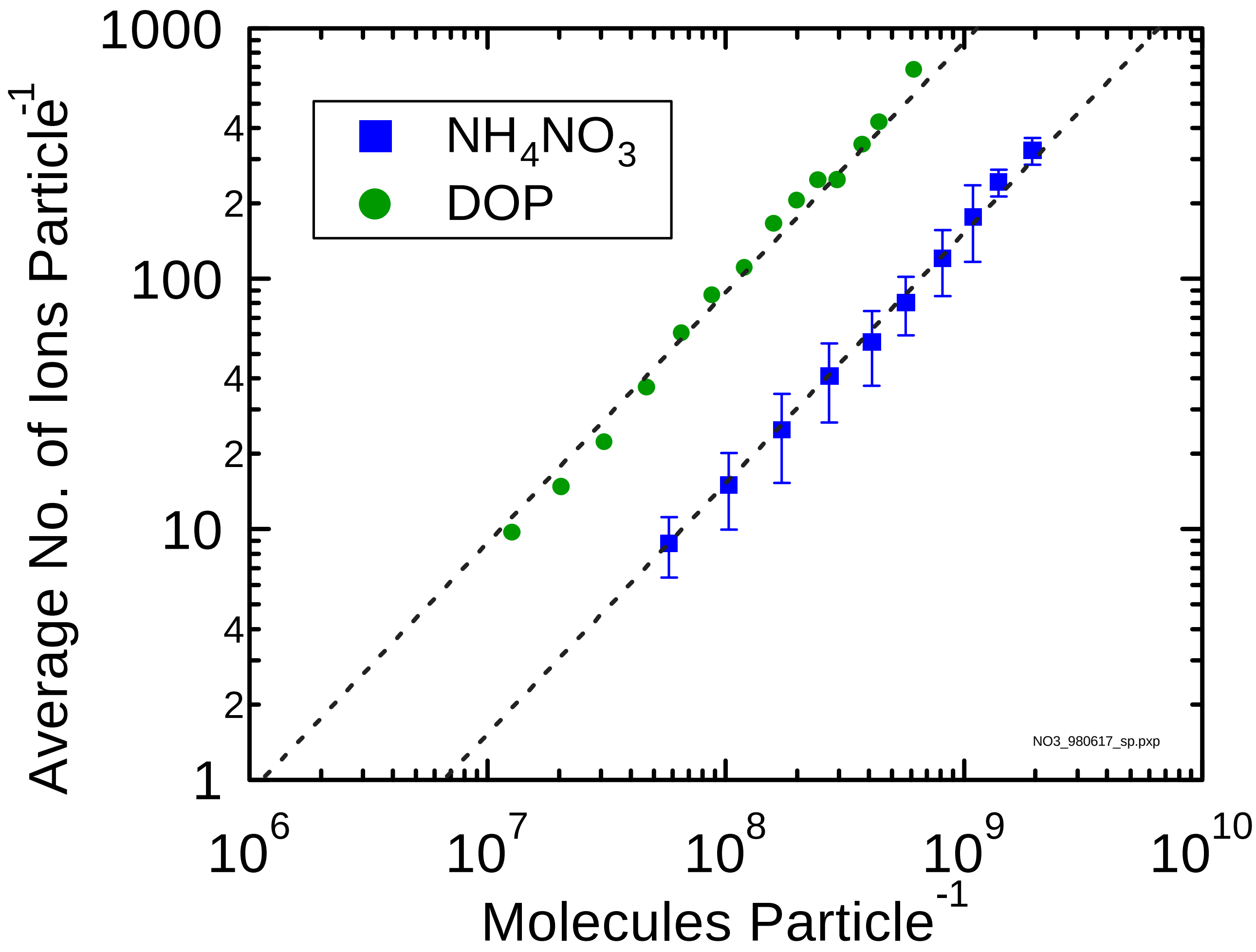
Particles vaporization events are sharply resolved in TOF space.

Fast Particle Vaporization *(<20μsec)*

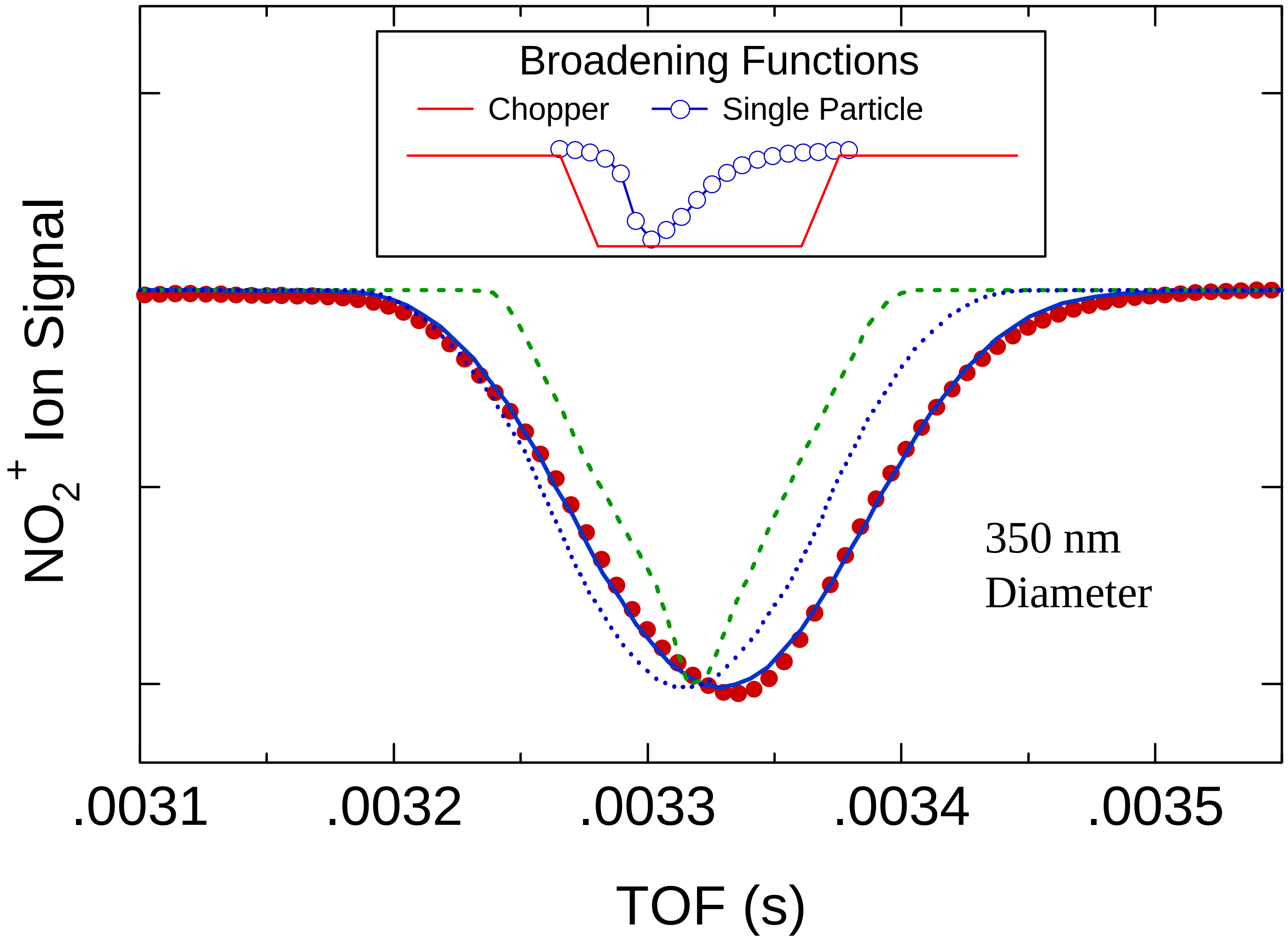


Average area of single particle signal scales linearly with particle mass

Single Particle Signal Varies Linearly with Particle Mass

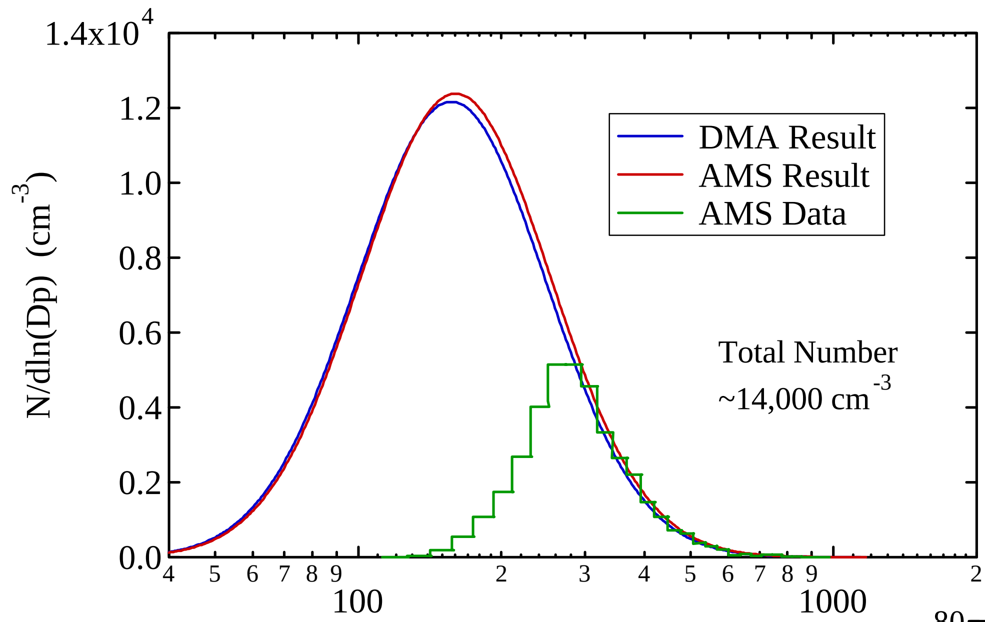


AMS Transfer Function



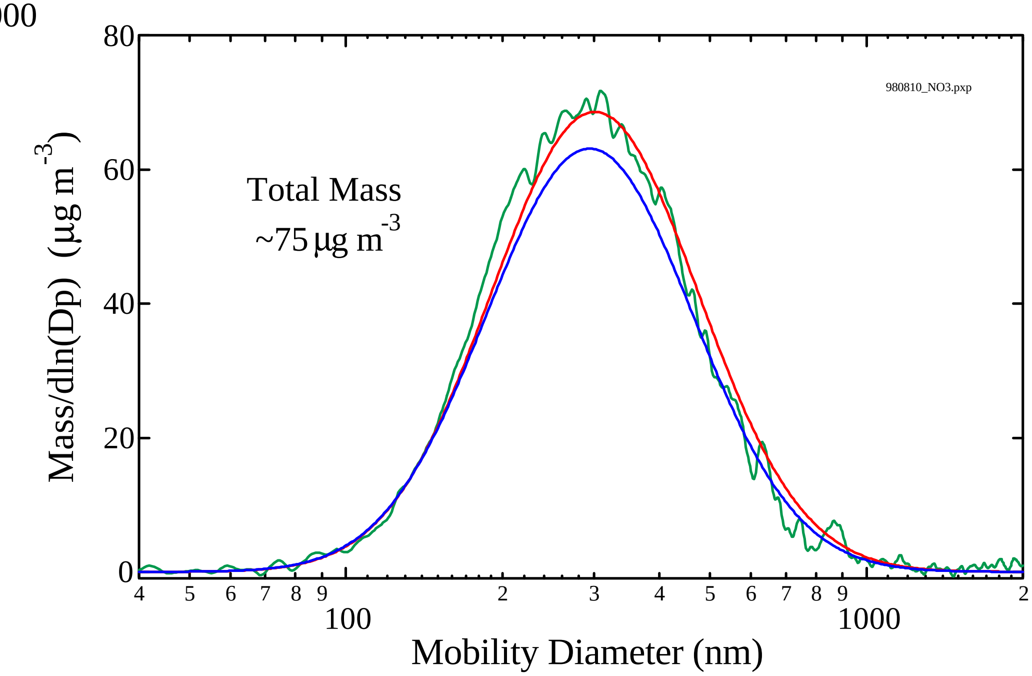
Broadening Effect of the Time Width of the Chopper Open Gate and the Particle Vaporization Time

AMS and DMA Data Inversion Results



Number Density

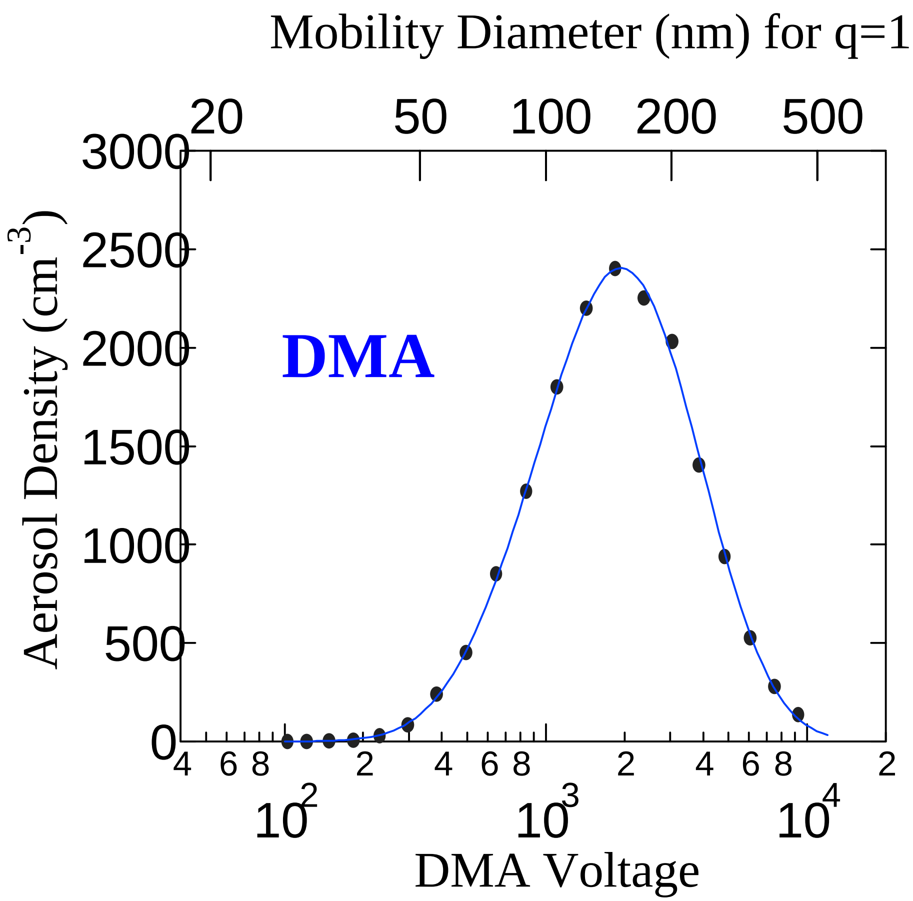
agrees within 2%

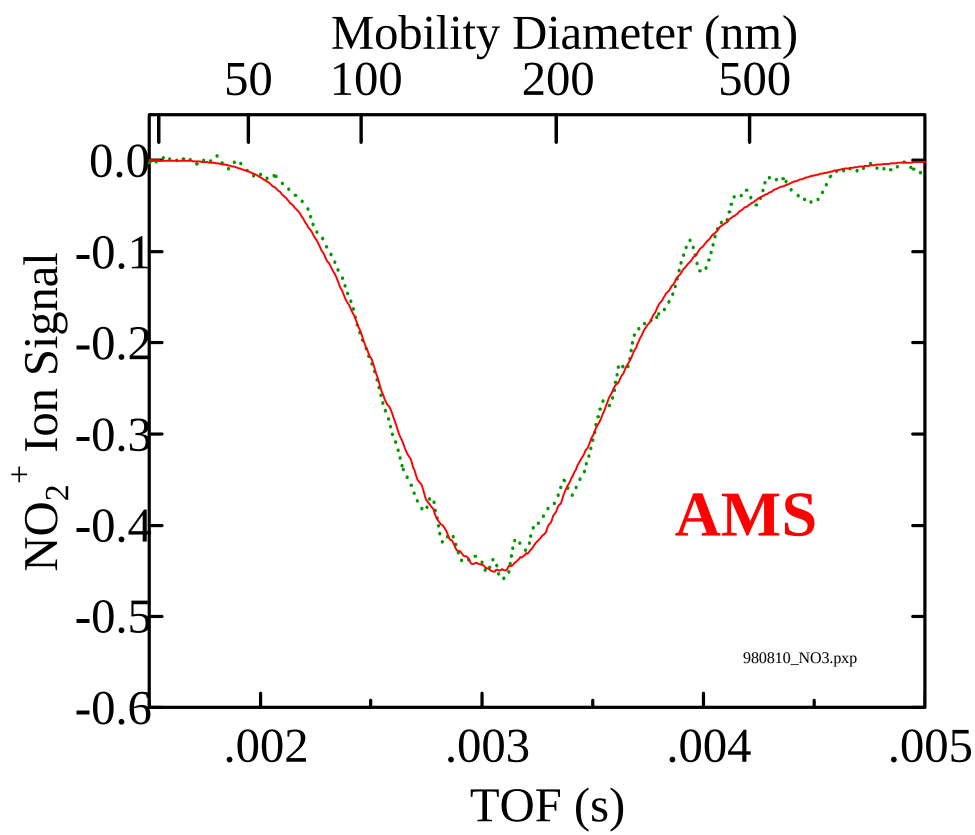


Particle Mass Loading

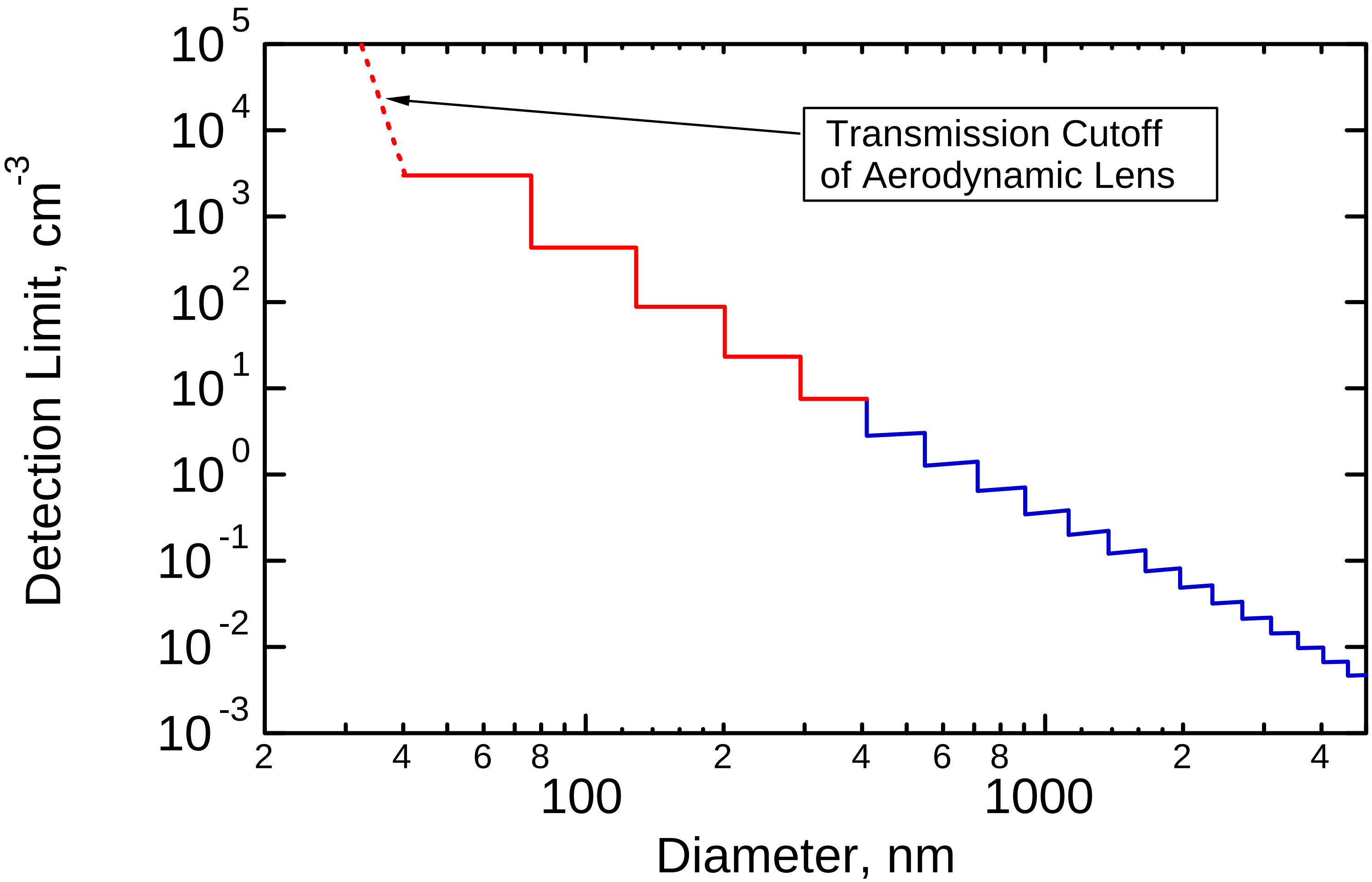
agrees within 8%

Same Polydisperse NH_4NO_3 Distribution Measured by DMA-CPC and by AMS





Resolution and Detection Limit

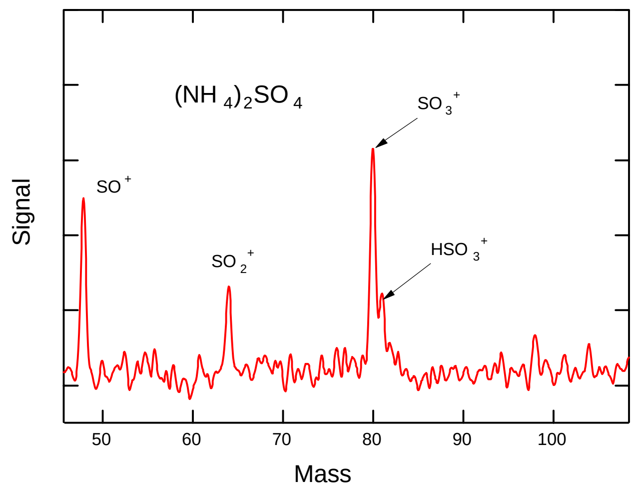


•Calculation based on 2% chopper duty cycle, 100second integration time, and detection limit of 0.1 µg m^{-3} (measured for pure NH_4NO_3 aerosol).
•Detection limit scales with the mass fraction of the ionized chemical fragment.
•Required integration/acquisition time scales with the number of sampled quadrupole masses.

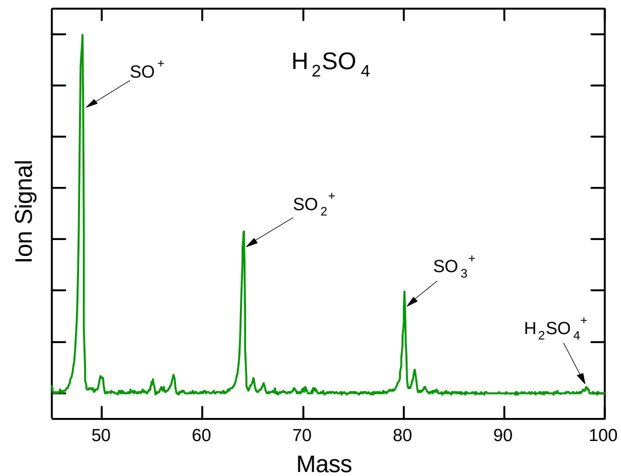
Sample Mass Spectra of Particulate Matter

Composition Information by Molecular Mass Spectrometry following Particle Vaporization on a Heated Surface and Electron Impact Ionization

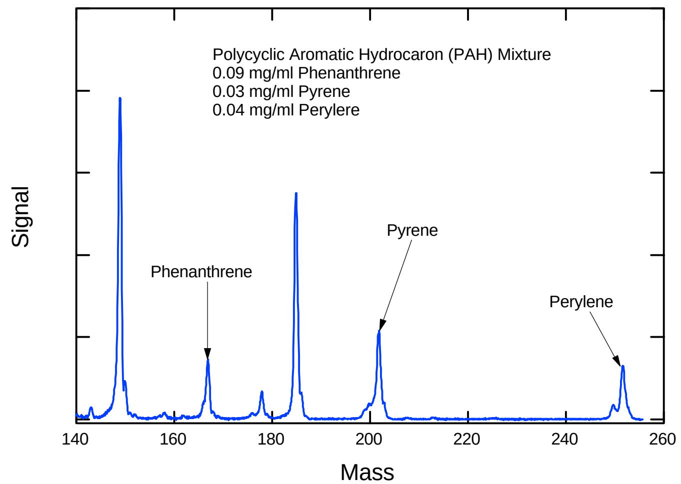
Ammonium Sulfate



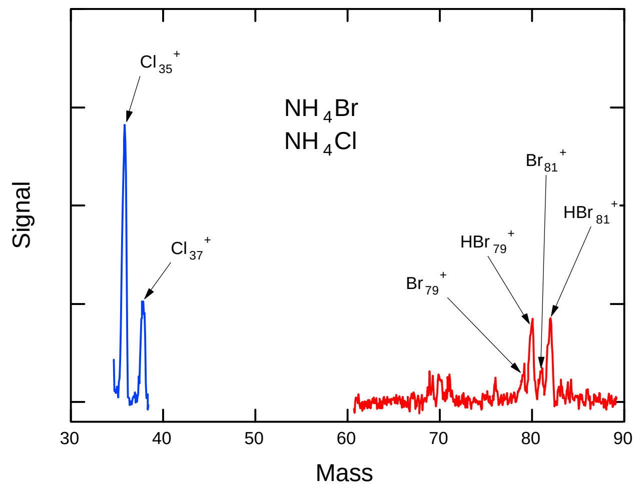
Sulfuric Acid



Polycyclic Aromatic hydrocarbon Mixture



Ammonium Chloride/ Ammonium Bromide



Aerosol Species Detected

Inorganic	Organic	Biological
H_2SO_4	DOP	Bovine albumin
NH_4NO_3	DOS	Bacillus Subtilis
$(NH_4)_2SO_4$	Perylene	
NH_4Cl	Phenanthrene	
NH_4Br	Pyrene	
KI	PSL	
KCl	Nicotine	
KBr		
NaCl		
NaI		
NaBr		
$NaNO_3$		

Factors Influencing Instrument Performance

Particles must vaporize to be detected.

Efficient detection limited to volatile and semi-volatile species.

Particles must vaporize efficiently (fast).

Influences TOF measurement and resolution of aerodynamic size determination.

Fragmentation of molecular species from the electron impact ionization process.

Different molecules can be detected at the same m/z ratio.